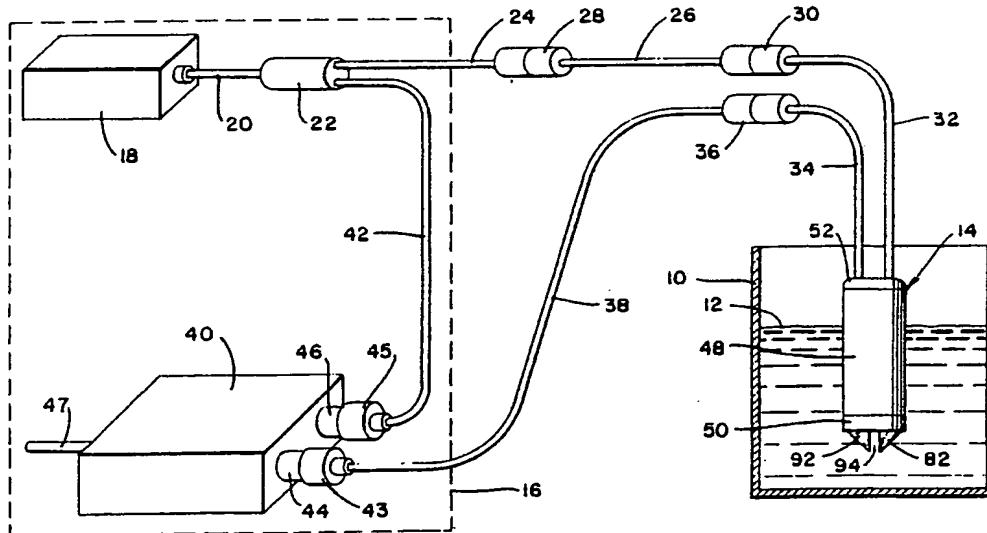




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>4</sup> : G01N 21/25, 21/85, G12B 17/02 G02B 6/32		A1	(11) International Publication Number: <b>WO 88/02109</b> (43) International Publication Date: 24 March 1988 (24.03.88)
(21) International Application Number: PCT/US87/01884 (22) International Filing Date: 3 August 1987 (03.08.87)		(74) Agents: ALKOV, Leonard, A. et al.; Hughes Aircraft Company, Post Office Box 45066, Bldg. C1, MS A126, Los Angeles, CA 90045-0066 (US).	
(31) Priority Application Number: 907,269 (32) Priority Date: 15 September 1986 (15.09.86) (33) Priority Country: US		(81) Designated States: AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, NL (European patent), SE (European patent).	
(71) Applicant: HUGHES AIRCRAFT COMPANY [US/US]; 7200 Hughes Terrace, Los Angeles, CA 90045-0066 (US). (72) Inventors: PESAVENTO, Philip, V. ; 1622 6th Street, Manhattan Beach, CA 90266 (US). STRAWBRIDGE, Joy, W. ; 5450 Butterfield Street, Camarillo, CA 93010 (US).		<p><b>Published</b>  <i>With international search report.  Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	

## (54) Title: SYSTEM FOR SENSING IONS IN AQUEOUS SOLUTION



## (57) Abstract

The system for sensing ions in aqueous solution such as an electroplating bath includes a light source (18) which delivers light including a selected wavelength through a series of optical fibers (20, 24, 26, 32) to probe (14). The probe is partially immersed in the solution (12) and the light is delivered through the solution in the space (94) between prisms (82, 92). The return light is conducted by optical fibers (32, 38) to detector or opto-electronic transducer (44). A portion of the original light is diverted by splitter (22) through fiber (42) to opto-electronic transducer (46) so that a comparison of the signals determines the amount of light in selected wavelength is absorbed in the solution due to ions thereon. The signal processing unit (40) is preferably enclosed in an electromagnetic protected area (16) to avoid the adverse EMI and corrosive atmosphere effects near the electroplating tank (10).

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

## SYSTEM FOR SENSING IONS IN AQUEOUS SOLUTION

1

BACKGROUND OF THE INVENTION

5 This invention is directed to a system for sensing specific ions in aqueous solution, including a corrosion resistant sensor for submersion in the aqueous solution, a fiber optic system to transmit illumination of a specific wavelength to the sensor, and a fiber optic system to transmit the absorption signal back to a detector which is located in a secure environment.

10 One particular environment in which the system is particularly useful is the determination of copper ion concentration in copper plating tanks. This determination has previously been accomplished by manually taking a sample of the plating solution and 15 testing the solution in equipment simulating the electro-plating environment, plating out the copper from the sample solution onto an electrode. The electrode was weighed before and after the plating operation to determine the amount of copper plated out to thus 20 derive the concentration of copper in the original plating solution. This analysis process of plating out the copper takes several hours, and the results are usually not known to the plating line operators in the plating shop for about six hours after the sample was 25 taken. If the copper ion concentration in the plating solution falls outside the range for good copper deposition, the plating will not meet the requisite quality standards. Printed circuit boards require copper plating to build up the circuit traces after the board 30 has been etched. If the deposited copper does not meet the requisite quality standards, the printed circuit boards must be scrapped. Thus, there is need to have current knowledge of the concentration of ions of

1 interest in plating solution so that ion concentration can be continuously corrected to maintain a solution from which top quality electroplating can be accomplished.

5

SUMMARY OF THE INVENTION

In order to aid in the understanding of this invention, it can be stated in essentially summary form that it is directed to a system for sensing ions in 10 aqueous solution. The system comprises a light source for emitting light of a selected wavelength, an optical probe for insertion into the aqueous solution for passing light through a portion of the aqueous solution, and a light detector for sensing the amount of light 15 that is passed through the aqueous solution, together with interconnecting optical fibers so that the light source and light detector can be placed in a protected environment.

It is a purpose and advantage of this invention 20 to sense ions in aqueous solution, particularly electroplating baths, in real time so that the plating solution can be continuously monitored and corrected to provide best quality plating.

It is another purpose and advantage of this 25 invention to provide a system which is connected together by means of fiber optics so that the optical probe may be inserted into the plating tank but the light source and light detector can be placed in an environment which is protected both from the chemical environment of the 30 plating tank and the electrical noise of the plating tank so that the system has a long life and accurate readout in a difficult environment.

Other purposes and advantages of this invention will become apparent from a study of the following 35 portion of this specification, the claims and the attached drawings.

## 1

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

FIG. 1 is a perspective view of the system  
5 of this invention, with parts broken away.

FIG. 2 is an enlarged side-elevational view  
of the optical probe, with parts broken away and parts  
taken in section.

FIG. 3 is a further enlarged section taken  
10 generally along line 3-3 of FIG. 2.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Electroplating tank 10 has an electroplating  
15 aqueous solution or bath 12 therein. In the preferred  
example, copper is the metal being plated out of the  
bath 12. Therefore, the bath 12 includes copper sulfate  
which is ionized into  $Cu^{++}$  and  $SO_4^{--}$ . The hydrated  
copper complex gives the solution its characteristic  
20 blue color. The blue color is caused by light absorption  
in the red or near infrared portion of the spectrum.  
The absorption peak is at 820 nanometers wavelength in  
the near infrared. With other things substantially  
equal, the amount of light at that wavelength absorbed  
25 over a fixed path length is proportional to the concen-  
tration of the copper ions in the bath 12.

The copper plating solution bath is a difficult  
environment in which to perform accurate measurements.  
The bath is highly acidic with a pH of less than 1.  
30 The typical composition of a copper plating bath is 80  
grams/liter of  $CuSO_4 \cdot 5H_2O$  (copper sulfate pentahydrate),  
10% by volume of  $H_2SO_4$  (sulfuric acid), 70 parts per  
million HCl (hydrochloric acid), 0.5% by weight of  
Gleam PCM (an organic wetting and brightening agent) in  
35 water as a solvent. The electroplating current is

1 full-wave rectified alternating current, without  
smoothing or filtering, which produces a great deal of  
electrical and magnetic noise in the ambient environment  
around the bath. Probe 14 must be configured to with-  
5 stand the chemical corrosion of the bath and must  
employ measurement and signal techniques which are not  
adversely influenced by the electrical and magnetic  
interference in the environment. While electron processing  
is an optimum way to analyze the signals, the fact that  
10 the hydrated copper complex has an absorption peak at  
820 nanometers wavelength and this peak is proportional  
to the copper complex in the copper plating solution  
12, optical sensing is an optimum sensing method.  
Furthermore, optical signal transmission is a desirable  
15 way to avoid the interference from the adverse electro-  
magnetic environment. Therefore, probe 14 is an optical  
probe connected to the electronic sensing equipment by  
means of fiber optic cables.

Referring to FIG. 1, an electromagnetically  
20 protected area 16 such as a screen room contains light  
source housing 18 which, in turn, has a light source  
therein which has a significant output at the 820 nano-  
meters wavelength. The area 16 protects against electro-  
magnetic interference (EMI) as well as against corrosive  
25 atmosphere. If distances are reasonable and losses  
minimal, a low power light source can be employed. In  
the present case, the distances and losses are designed  
so that a light-emitting diode having an output at  
820 nanometer wavelength is employed. The optical  
30 output appears in optical fiber 20 which delivers the  
light to optical splitter 22. A principal part of the  
optical output from splitter 22 is delivered to optical  
fiber 24 which serves as the input signal to probe 14.  
In the preferred example, 90% of the optical power in  
35 fiber 20 is delivered to fiber 24. Fiber 26 is a

- 1 continuation thereof coupled by coupling 28. Fiber 26 is coupled through coupling 30 to the input fiber 32 to probe 14. The signal fiber 34 contains the output signal from probe 14. The signal fiber 34 is connected 5 through coupling 36 to signal fiber 38 which is connected into the electromagnetic interference protected area 16 and is connected to the processing unit 40. The feedback fiber 42 carries the balance of the source light in fiber 20 and is also connected to processing unit 14.
- 10 All fibers are single fibers and are operated as multi-mode optical fibers. Optical splitter 20 is conveniently formed with the fiber 20 passing straight through to come out as fiber 24 and with the fiber 42 lying thereagainst and partially fused thereto so that the feedback 15 fiber 42 receives 10% of the original light.

Processing unit 40 has optical detectors 44 and 46 respectively connected to receive the light from fibers 38 and 42. These detectors convert the optical signals to respective electrical signals. The 10% 20 signal feedback in feedback fiber 42 is provided so that changes in light source can be incorporated into the evaluation of the signal in fiber 38. The electronic output line 48 delivers a signal which is related only to the absorption found by probe 14.

25 When the light source is monochromatic, such as from a laser or a light-emitting diode, filters are not needed for achieving a narrow bandwidth source at 820 nanometers wavelength. For white light sources, including arc lamps and incandescent lamps, a narrow bandwidth 30 filter will be needed. It is preferable that the filters 43 and 45 be placed between the fibers 38 and 42 and detectors 44 and 46 respectively so that the filters operate at a lower energy with multimode transmission.

1 Photodetectors which can be utilized at 820 nanometers wavelength include solid state detectors and vacuum photomultiplier devices. These devices convert the optical input signal to an electrical output signal.

5 Solid state detectors can be used for short and medium distances where the distance between probe 14 and processing unit 14 is in the range of 10 to 100 meters. Over very long distances, such as 100 meters to 10 kilometers, photomultiplier tubes would be preferred

10 because of their greater sensitivity. The greater sensitivity of photomultiplier tubes can be used to advantage with fibers of short to medium length, where very low concentrations of hydrated copper sulphate are to be detected. Light source fluctuations due to power

15 line transients and temperature drift cause light source fluctuations, and these fluctuations will affect the chemical analysis unless light source feedback is employed. Splitting the beam through fiber 42 and utilizing a sample of the light source fed directly to

20 the detector 46 eliminates that problem.

The probe 14 serves as an interface between the plating solution 12 and the light in the optical fibers 32 and 34. Since the plating solution 12 is an adverse environment for structures, in view of its acidity, the

25 structure of the probe is carefully configured to provide a reasonable life for the probe. Casing 48 is closed on its front end by front plate 50 and its upper end by cap 52. As is seen in FIG. 1, the cap has openings therein for passage therethrough of the fibers 32 and 34. The cap is sealed around the fibers. Front plate 50 has threaded openings 54 and 56 therein. As seen in FIG. 3, lens carrier 58 is screwed into the opening 56. Lens carrier 58 has screw threads 60 which engage in threaded opening 56 and has a shoulder 62 which engages

30 against the top surface of front plate 50 so that the

35

1 lens carrier 58 can be firmly screwed into place and sealed to prevent leakage through the opening 56. Connection adaptor 64 carries fine threads on its lower end which engage in the threaded recess 66 in the top 5 of lens carrier 58. Lock nut 68 engages on more coarse threads 70 on the upper end of the adaptor 64. The threads 70 are configured to receive connector nut 72. Connector nut 72 engages on the halves 73 and 75 of the clamp sleeve which clamp to the outer end of input 10 fiber 32. Fine threads 66 are provided so that up and down adjustment can be made of the connector adaptor 64 to control the position of the end 74 of input fiber 32.

In the present case, the end is shown with a 15 small gap between the fiber and the flat side of hemispherical lens 76. The lens is secured against shoulder 78 in the bottom of lens recess 80. Prism 82 is mounted on and sealed against the front of front plate 50. Prism 82 is a conventional 5-sided orthogonal prism 20 with two sides at right angles and with the angular face preferably at a 45° angle with respect to both orthogonal faces. Input face 86 is at right angles to output face 88. The output face 88 is spaced from and parallel to the input face 90 of prism 92. The input 25 and output faces define space 94 therebetween. Behind lens 92 is a lens carrier 96 which is identical to lens carrier 58 and a connection adaptor 98 identical to connection adaptor 64 to thus connect the prism 92 to signal fiber 34.

30 When the probe 14 is placed in a plating bath solution 12, as seen in FIG. 1, and the system is energized, light at 820 nanometers is delivered to fiber 32 and the fiber 32 delivers it through prism 82 and across gap 94. The plating bath solution 12 occupies 35 the gap 94 and the amount of light transmitted across

1 the space 94 is a function of the absorption of the  
bath materials in that part of the spectrum. The 820  
nanometer wavelength is chosen because it is the peak  
absorption of the hydrated copper complex in the bath.  
5 Therefore, the amount of light absorbed and, consequently,  
the amount of light transmitted into prism 92 is a  
function of the concentration of the hydrated copper  
complex. The signal in signal fiber 34 and the signal  
in signal fiber 38 to the optical detector 44 is thus  
10 related to the amount of hydrated copper complex in the  
bath. As previously described, changes in the light  
source are compensated by the light in the feedback  
fiber 42. The optical information is converted to  
electronic signals in detectors 44 and 46, and the  
15 electronic signals are processed in unit 40 to provide  
a signal in output line 47 which is a signal to the  
operator giving him the state of concentration of the  
hydrated copper complex in the bath.

The preferred structural embodiment of this  
20 invention has been described as being utilized for the  
sensing of copper ion concentration in a copper plating  
bath. By choice of a particular wavelength to be  
transmitted across the gap 94, and related light source,  
filter and detector characteristics, the system can be  
25 used in other baths to detect other materials. Tin-  
lead electroplating baths employ Peptone to improve the  
plating quality. Peptone is an animal organic material  
which acts as a wetting agent and as a brightener in  
such baths. Solder is electroplated onto solder pads  
30 on which electronic components will be surface-mounted.  
Solder plating baths contain several hazardous materials  
so that taking samples requires extreme caution.  
Fluboric acid ( $HBF_4$ ) is one of the few materials in  
which eutectic tin-lead solder will dissolve. Without  
35 the addition of Peptone, the tin-lead plates out with a  
grey surface appearance and is brittle in bend testing.

- 1 The addition of Peptone eliminates the brittleness and causes the tin-lead solder to plate out with a bright surface.

Peptone is a complex organic, and it is not known which component or components thereof cause the improvement in plating characteristics. However, it has been determined that the organic constituents in the Peptone which are favorable to plating absorb ultraviolet light in the range of 200 to 360 nanometers. Thus, by employing the probe 14 the system, the effective Peptone concentration can be measured. When the probe 14 is used in this range, the light source in housing 18 is preferably a deuterium arc lamp, which has a significant ultraviolet output. The optical splitter, fibers and probe are the same as previously described. Filters 43 and 45 pass ultraviolet in the range of 200 to 360 nanometers, and preferably in the more narrow range of 300 to 340 nanometers. In this narrower range, it has been determined that there was a larger change in detected light absorption with changes in Peptone concentration. In this way, real time analysis of Peptone in lead-tin solder plating solutions is achieved, to maintain solder plating solution balance, increase production efficiency, and decrease danger to personnel by eliminating sampling. This advantage of successful sampling is achieved by employment of the clad single fibers so that an adequate distance between the probe and the electromagnetic interference protected instrumentation can be achieved.

This invention has been described in its presently contemplated best mode, and it is clear that it is susceptible to numerous modifications, modes and embodiments within the ability of those skilled in the art and without the exercise of the inventive faculty. Accordingly, the scope of this invention is defined by the scope of the following claims.

CLAIMSWhat is Claimed is:

- 1        1. A system for sensing ions in aqueous solution
- 2 comprising:
- 3            a light source which produces light at a
- 4 selected wavelength;
- 5            a probe for insertion partway into an aqueous
- 6 solution;
- 7            an optical fiber connecting said light source
- 8 with said probe;
- 9            a first optical detector;
- 10          an optical fiber connecting said probe with
- 11 said first optical detector;
- 12          signal processing means connected to said
- 13 optical detector for processing an electrical analog of
- 14 the optical signal received by said first detector;
- 15          electromagnetic interference protection
- 16 positioned around said processing means for protecting
- 17 said processing means from ambient electromagnetic
- 18 interference;
- 19          said probe having a light path therethrough
- 20 and having a space in said light path to be occupied by
- 21 the aqueous solution so that light at selected frequency
- 22 passes into said probe across said space and back to
- 23 said first detector so that the absorption of light by
- 24 aqueous solution in said space affects the light
- 25 delivered to said first detector and affects the signal
- 26 processed by said signal processing unit.

1           2. The system of Claim 1 wherein there is a  
2 second optical detector connected to said processing  
3 unit and there is an optical fiber connected between  
4 said light source and said second optical detector to  
5 feed to said processing unit a signal corresponding to  
6 said light source.

1           3. The system of Claim 2 wherein said probe  
2 carries first and second prisms and said first and  
3 second optical fibers are respectively connected to  
4 said first and second prisms, said space being  
5 positioned between prism faces.

1           4. The system of Claim 3 wherein a first lens  
2 is positioned between said first fiber and said first  
3 prism and a second lens is positioned between said  
4 second fiber and said second prism.

1           5. The system of Claim 1 wherein said probe  
2 comprises a hollow casing and a front plate secured  
3 to the front end of said probe to enclose the front  
4 end of said probe, said front plate having first and  
5 second openings therein, said first and second prisms  
6 respectively covering and closing said first and second  
7 openings.

1           6. The system of Claim 5 wherein first and  
2 second connection adaptors are respectively attached  
3 to said front plate interiorly of said casing and in  
4 respective alignment with said first and second openings  
5 in said front plate, said first and second optical  
6 fibers being disconnectably attached to said first and  
7 second connection adaptors.

1           7. The system of Claim 6 wherein there are  
2 first and second lenses respectively positioned with  
3 respect to said first and second prisms and said  
4 connection adaptors are respectively threaded to permit  
5 focus adjustment of said respective first and second  
6 fibers with respect to said first and second lenses to  
7 optimize optical coupling between said fibers and said  
8 prisms.

1           8. The system of Claim 7 wherein there is a  
2 second optical detector connected to said processing  
3 unit and there is an optical fiber connected between  
4 said light source and said second optical detector to  
5 feed to said processing unit a signal corresponding to  
6 said light source.

1           9. The system of Claim 8 wherein said probe  
2 carries first and second prisms and said first and  
3 second optical fibers are respectively connected to  
4 said first and second prisms, said space being  
5 positioned between prism faces.

1           10. A probe for partial insertion into an aqueous  
2 solution, comprising:  
3                 a hollow casing having a front end and a cap  
4 end;  
5                 a front plate enclosing said front end of said  
6 casing, said front plate having an outside and an  
7 inside, said front plate having first and second openings  
8 therethrough from said outside to said inside;  
9                 first and second prisms mounted on the  
10 outside of said front plate to respectively cover said  
11 first and second openings therein, said prisms having  
12 faces facing each other and spaced from each other to  
13 define a space therebetween;

14 first and second optical fibers;  
15 means for mechanically and optically  
16 connecting said first and second optical fibers with  
17 respect to said first and second openings in said front  
18 plate so that light in said first fiber can illuminate  
19 said first prism and direct light across said space  
20 between said first and second prisms and light received  
21 by said second prism and directed into said second  
22 fiber as modified by the optical absorption of the  
23 material within said space.

1               11. The probe of Claim 10 wherein first and  
2 second lens carriers are respectively secured over said  
3 first and second openings in said front plate on the  
4 interior side of said lens plate, said first and second  
5 optical fibers being mounted with respect to said first  
6 and second lens carriers.

1                   12. The probe of Claim 11 wherein first and  
2 second lenses are respectively mounted in said first  
3 and second lens carriers to focus light between said  
4 prisms and said fibers.

1               13. The probe of Claim 12 wherein first and  
2 second connection adaptors are respectively threadedly  
3 engaged in said first and second lens carriers, said  
4 first and second optical fibers being respectively  
5 attached to said first and second connection adaptors.

1           14. The probe of Claim 13 wherein there are  
2   first and second connection adaptors respectively  
3   threaded with respect to said first and second lens  
4   carriers, said first and second fibers being respectively  
5   attached to said first and second connection adaptors  
6   so that the position of said first fiber can be adjusted  
7   with respect to said first lens by threaded engagement  
8   of said first connection adaptor within said first lens  
9   carrier and said second fiber can be adjusted with  
10   respect to said second lens by threaded engagement  
11   of said second connection adaptor within said second  
12   lens carrier.

1           15. The probe of Claim 14 wherein first and  
2   second lock nuts respectively interengage between said  
3   first and second connection adaptors and said first and  
4   second lens carriers.

1           16. The method of sensing ions in aqueous  
2   solutions comprising the steps of:  
3           positioning first and second opto-electronic  
4   transducers in an electromagnetic interference protected  
5   environment, together with a processing unit for  
6   comparing and processing electronic signals from the  
7   first and second transducers;

8           providing light of a selected wavelength  
9   corresponding to an absorption peak of the ion desired  
10   to be sensed in an aqueous solution;

11           delivering the light through a single  
12   optical fiber to a probe;

13           partially immersing the probe in the aqueous  
14   solution so that the light is delivered through a  
15   portion of the aqueous solution;

16           delivering light from which a portion of  
17   the energy has been absorbed in the solution through an  
18   optical fiber to the first opto-electronic transducer; and

19           delivering a portion of the light from the  
20 light source through an optical fiber directly to a  
21 second transducer so that comparison of the outputs of  
22 the first and second transducers by the processor  
23 signals the amount of light absorbed in the aqueous  
24 solution.

1           17. The method of Claim 16 wherein the step of  
2 delivering light through the aqueous solution comprises  
3 the step of:

4           delivering light from the source fiber to  
5 a first prism which has a face exposed to the solution  
6 and collecting the light from the solution by means of  
7 a second prism having a face exposed to the solution  
8 and facing the exposed face of the first prism.

1           18. The method of Claim 17 wherein the step of  
2 producing light comprises the step of:

3           producing light at substantially 820  
4 nanometers wavelength, and the step of immersing the  
5 probe comprises:

6           immersing it into an electroplating solution  
7 containing hydrated copper complex.

1           19. The method of Claim 17 wherein the step of  
2 producing light comprises the step of:

3           producing light in the range of 300 to 360  
4 nanometers wavelength, and the step of immersing the  
5 probe comprises:

6           immersing it into an electroplating solution  
7 containing Peptone.

FIG. 1

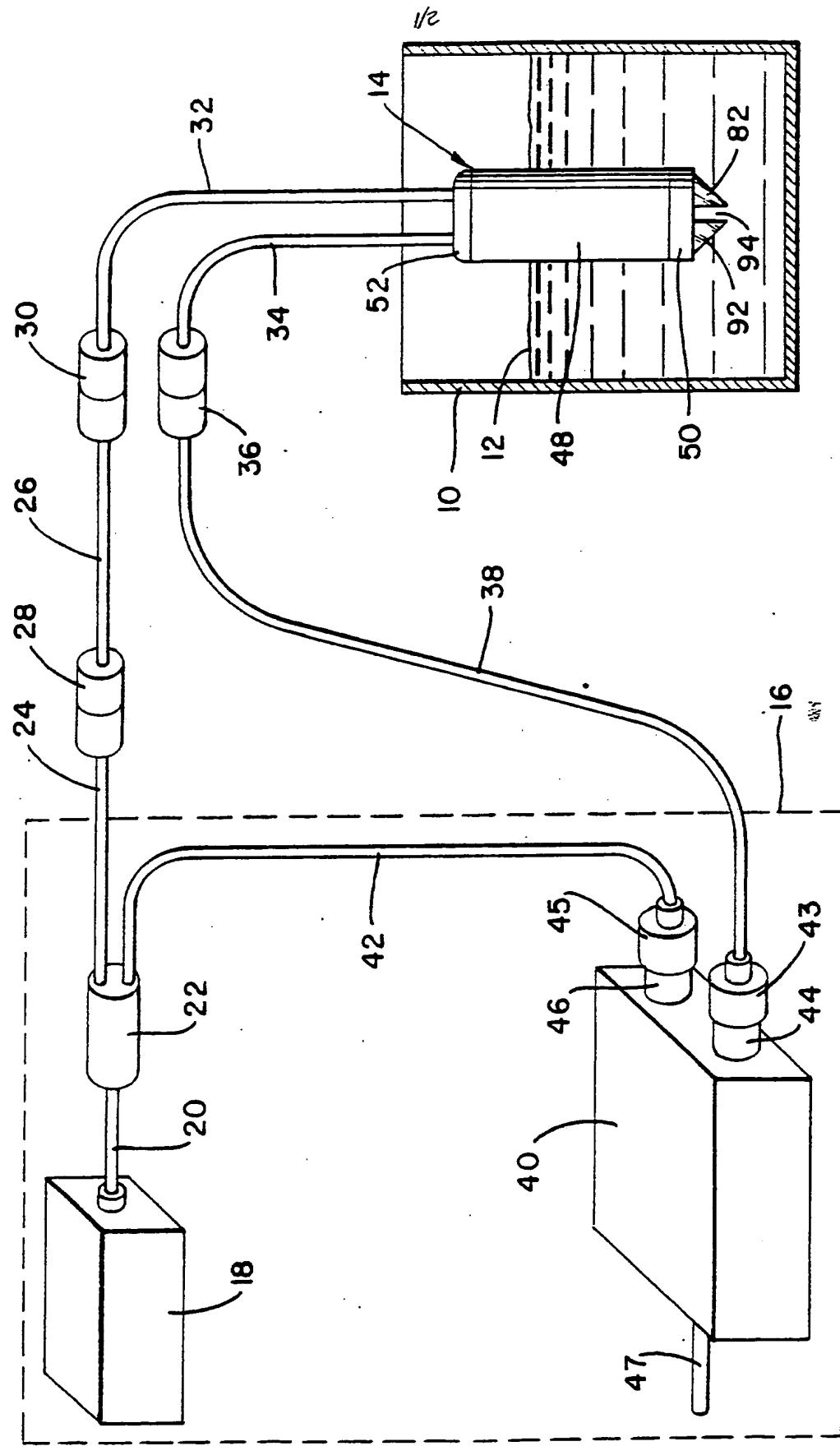


FIG. 2

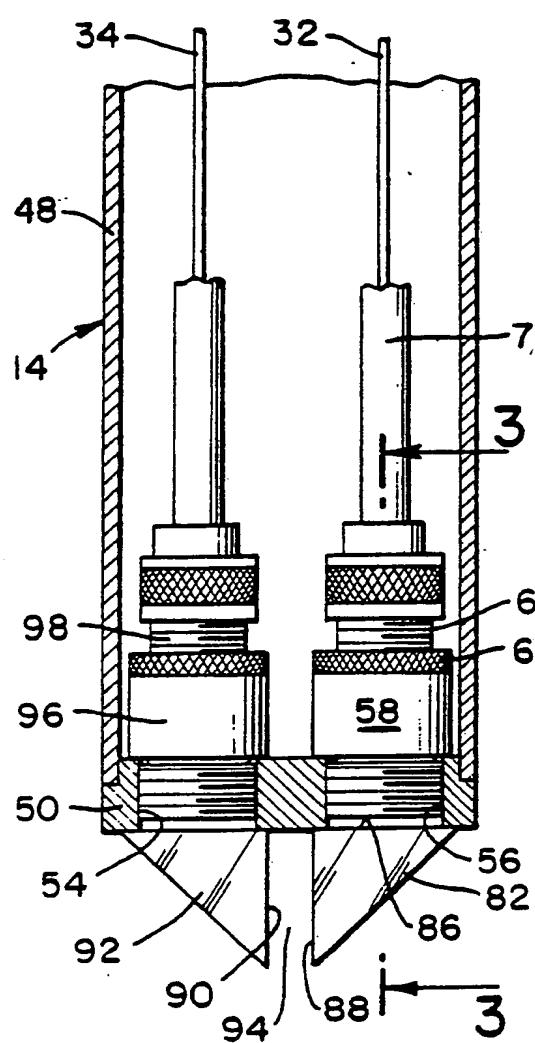
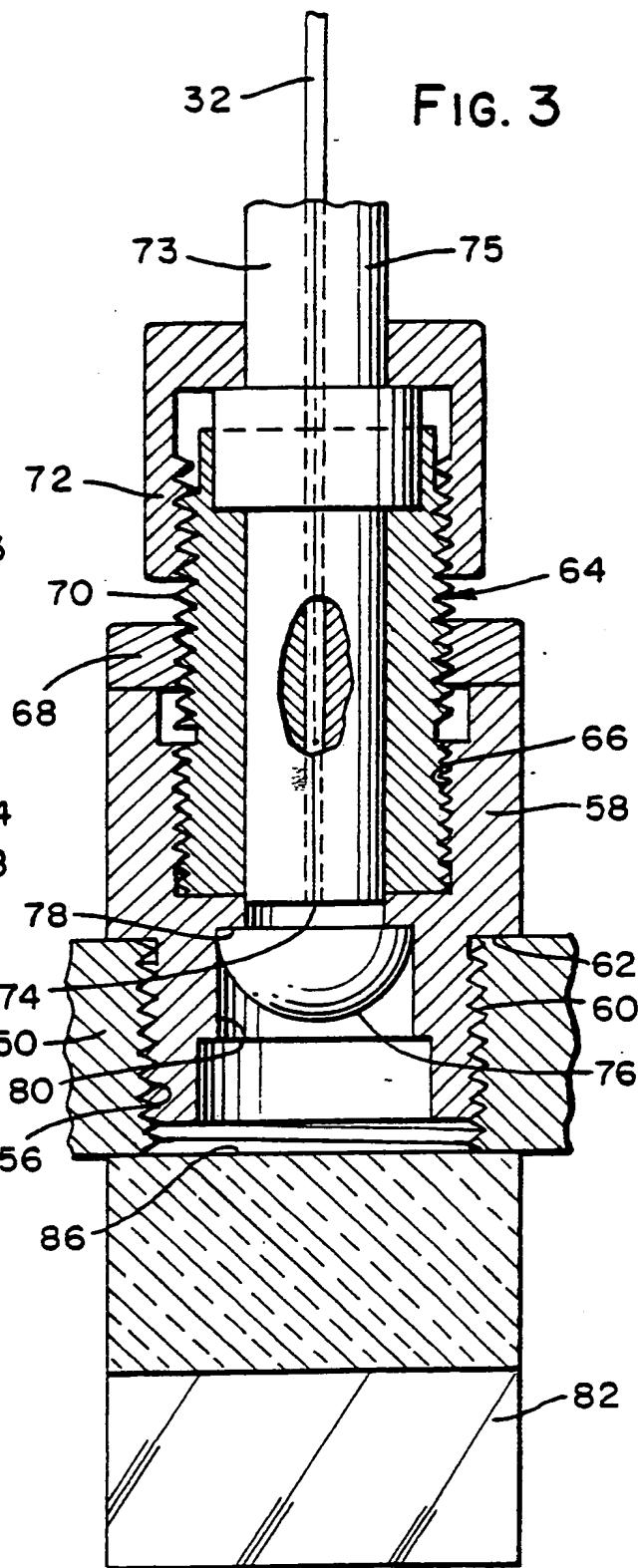


FIG. 3



# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/01884

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>4</sup> : G 01 N 21/25; G 01 N 21/85; G 12 B 17/02;  
G 02 B 6/32

## II. FIELDS SEARCHED

Minimum Documentation Searched \*

Classification System	Classification Symbols
IPC <sup>4</sup>	G 01 N 21/00; G 02 B 6/00; G 12 B 17/00

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	NL, A, 8400451 (STICHTING WATERBOUW-KUNDIG LAB.) 2 September 1985, see figure	1,3,16,17
A	--	2,9,10
Y	F.A. van Goor: "Generation of ultra-short CO <sub>2</sub> lasers pulses by mode-locking techniques", 1984, F.A. van Goor (Enschede, NL), pages 5,6, 106-111, see page 110, lines 12-16	1,3,16,17
A	US, A, 4241738 (LUBBERS et al.) 30 December 1980, see column 3, lines 33-51; column 6, lines 7-29; figure 2	2,8,16
A	Patent Abstracts of Japan, volume 7, no. 32, (P-174)(1177) 8 February 1983, & JP, A, 57-186158 (SUNTORY K.K.) 16 November 1982	3,5,9,10,17
A	EP, A, 0047094 (ORIEL) 10 March 1982, see figures 1,5; page 15, lines 3-19; page 25, lines 2-14	5,10 . /.

\* Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

16th November 1987

Date of Mailing of this International Search Report

11 JAN 1988

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

M. VAN MOL

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Applied Optics, volume 20, no. 18, September 1981, (New York, US), A. Nicia: "Lens coupling in fiber-optic devices: efficiency limits", pages 3136-3145, see page 3136; figure 1	4,7,11,12
A	Patent Abstracts of Japan, volume 3, no. 64, (E-114) 31 May 1979, & JP, A, 54-42161 (FUJITSU K.K.) 4 March 1979	4,7,11,12
A	Patent Abstracts of Japan, volume 8, no. 129, (P-280)(1566) 15 June 1984, & JP, A, 59-31904 (SUMITOMO) 21 February 1984	4,7,11-15
A	GB, A, 2141537 (SHIPLEY COMPANY INC.) 19 December 1984, see page 2, lines 20-44; figure 1	1,18
A	Electro-Optical Systems Design, volume 13, no. 2, February 1981, (Chicago, US), R.A. Munsinger: "Fiber-optic colorimetry", pages 43-47	
A	Electronic Design, volume 30, no. 25, December 1982, (Denville, US) V. Biancomano: "Connector workshop addresses EMI, shielding standards", page 38	

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 8701884  
SA 18400

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on 11/12/87  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
NL-A- 8400451	02-09-85	None		
US-A- 4241738	30-12-80	FR-A- 2394788 DE-A- 2726606	12-01-79 21-12-78	
EP-A- 0047094	10-03-82	CA-A- 1172058	07-08-84	
GB-A- 2141537	19-12-84	FR-A- 2547655 DE-A- 3409003 JP-A- 60040935	21-12-84 20-12-84 04-03-85	